



## Products distribution during the gas phase photocatalytic oxidation of ammonia over the various titania based photocatalysts

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### ABSTRACT

The adsorption and photooxidation of gaseous ammonia have been investigated by the FTIR spectroscopy method in a static reactor using TiO<sub>2</sub> and modified TiO<sub>2</sub> as photocatalysts. Two types of modified TiO<sub>2</sub> were tested: TiO<sub>2</sub> impregnated with transition metal oxides (NiO, V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>) and TiO<sub>2</sub> doped with noble metals like Ag, Au, Pt, Pd by the chemical and photochemical deposition methods. Molecular nitrogen, NO<sub>3</sub><sup>-</sup>, N<sub>2</sub>O and water were found as the major final products of ammonia photocatalytic oxidation (PCO). One of the purposes of the current study was to minimize the N<sub>2</sub>O formation during PCO. The pure unmodified TiO<sub>2</sub> (anatase, S<sub>BET</sub> ~ 350 m<sup>2</sup>/g) turned out to be the best photocatalyst for this purpose giving only 7% of initial NH<sub>3</sub> quantity converted into N<sub>2</sub>O. Long-term experiments were carried out to determine the photocatalysts stability in PCO of NH<sub>3</sub>. All the catalysts exhibited stable performance; the rate of deactivation was low due to the transformation of NH<sub>3</sub> nitrogen mainly into N<sub>2</sub>. Only ≈30% of initial NH<sub>3</sub> quantity was oxidized into HNO<sub>3</sub> which was adsorbed on the catalysts surface in all cases.

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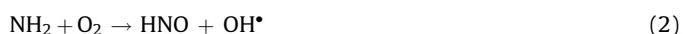
### 1. Introduction

Ammonia is the major air pollutant in the production of nitrogen fertilizers, agriculture, stock-breeding and especially poultry farming. Agricultural workers are exposed to huge ammonia concentrations resulting in numerous on-the-job respiratory diseases [1]. In addition, NH<sub>3</sub> is evolving from the urea containing antifreeze admixtures used for the depression of concrete freezing point in the building construction. So it is today an actual problem of air purifying from ammonia. A well-known TiO<sub>2</sub> mediated photocatalytic oxidation (PCO) method was chosen for this purpose for its universality and ability to mineralize almost any acescent substance [2,3]. Titanium dioxide is well known as a photocatalyst for the elimination of environmental pollutants and is a harmless white powder [4,5]. The TiO<sub>2</sub> photocatalyst absorbs photons with wavelengths below 400 nm and promotes redox reactions on its surface. The photocatalytic activity of TiO<sub>2</sub> was applied for NO<sub>x</sub> removal [6], water splitting [7], decomposition of VOC [8], etc., on a laboratory scale.

Italian scientists [9] demonstrated significant decrease of gaseous NH<sub>3</sub> concentration in a farrowing room as a result of TiO<sub>2</sub> mediated photocatalytic oxidation. TiO<sub>2</sub> was sprinkled on the

inside walls of the farrowing room and the irradiation was conducted by the 12 36 W UVA lamps. Dong et al. [10] tested the TiO<sub>2</sub> (Degussa P-25) supported on the woven fabrics for the removal of indoor ammonia.

According to the previous studies [11,12] nitrous oxide (N<sub>2</sub>O) should form as one of the final products during NH<sub>3</sub> PCO. The N<sub>2</sub>O formation occurs as a result of hyponitrous acid decomposition which in turn forms in the following sequences of reactions:



Nitrous oxide could form not only during the ammonia PCO but also other N-containing species like unsymmetrical dimethylhydrazine (H<sub>2</sub>N-N(CH<sub>3</sub>)<sub>2</sub>) which was reported in our previous work [13].

N<sub>2</sub>O is an important greenhouse gas with a lifetime of about 150 years in the atmosphere. It has about 310 times higher greenhouse potential than CO<sub>2</sub> [14], and contributes to the destruction of the ozone layer in the stratosphere [15]. N<sub>2</sub>O destruction occurs in the stratosphere by photolysis and oxidation and it is also an important source of stratospheric nitrogen oxides (NO<sub>x</sub>) which initiate a chain of cyclic reactions leading to ozone destruction [16,17]. In this way the limitation of N<sub>2</sub>O emissions has become a

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significant target in the control of anthropogenic emissions. So the first purpose of present study was to find the most suitable photocatalysts which minimize the N<sub>2</sub>O output during NH<sub>3</sub> PCO. Another subject for investigation was the photocatalysts stability during numerous cycles of NH<sub>3</sub> PCO.

## 2. Experimental

### 2.1. Materials

The ammonia (gas 99.8%), (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> (high-purity grade, REACHIM), Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (high-purity grade, REACHIM), NH<sub>4</sub>VO<sub>3</sub> (high-purity grade, REACHIM), Ni(NO<sub>3</sub>)<sub>2</sub> (high-purity grade, REACHIM), AgNO<sub>3</sub> (high-purity grade, REACHIM), H<sub>2</sub>SO<sub>4</sub> (high-purity grade, REACHIM), EtOH (high-purity grade, Hippocrat), H<sub>2</sub>PtCl<sub>6</sub> and HAuCl<sub>4</sub> (REACHIM) were used as supplied without further purification. Distilled water purified with Bärnsted "Easy pure II" ultra pure water system ( $\Omega = 18.2 \text{ M}\Omega/\text{cm}$ ) was used in all syntheses.

TiO<sub>2</sub> (Sachtleben Chemie, 100% anatase,  $S_{\text{BET}} = 347 \text{ m}^2/\text{g}$ , average pore diameter 4.9 nm) was used as pure photocatalyst and as further starting agent for the synthetically modified photocatalyst.

### 2.2. Modification of the TiO<sub>2</sub> surface

Different TiO<sub>2</sub> based photocatalysts were synthesized in the present work by TiO<sub>2</sub> impregnation with transition metal oxides (NiO, V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>) and TiO<sub>2</sub> doping with noble metals like Ag, Au, Pt, Pd by the chemical and photochemical deposition methods.

TiO<sub>2</sub> impregnation by metal oxides was conducted according to the following method. A 5 g of TiO<sub>2</sub> was placed in a 150 ml round-bottom flask and a 100 ml of aqueous solution with necessary metal salt (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>, NH<sub>4</sub>VO<sub>3</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>) was added. Concentrations of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>, NH<sub>4</sub>VO<sub>3</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> were equal to  $3.12 \times 10^{-3}$ ,  $3.47 \times 10^{-3}$ ,  $5.5 \times 10^{-3}$ ,  $6.67 \times 10^{-3} \text{ M}$  correspondingly so that after the mild water evaporation at 40 °C in the Petri dish and subsequent powder annealing at 770 K for 3 h the metal oxides content should be equal to 1, 0.1 and 0.01 wt.% for each of Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, MoO<sub>3</sub>/TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> and NiO/TiO<sub>2</sub> catalysts.

Ag, Au and Pt metals deposition were conducted by the TiO<sub>2</sub> impregnation with AgNO<sub>3</sub>, HAuCl<sub>4</sub> or H<sub>2</sub>PtCl<sub>6</sub> corresponding water solutions with subsequent reduction (chemical or photo-assisted). This procedure was described in detail previously [18]. There were synthesized Ag/TiO<sub>2</sub> and Au/TiO<sub>2</sub> photocatalysts containing 1 wt.% of Ag or Au by the photo-assisted reduction method and Ag/TiO<sub>2</sub>, Au/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> photocatalysts containing 1 wt.% of Ag or Au and 0.5 wt.% of Pt by the chemical reduction method.

### 2.3. FTIR in situ experiments

All TiO<sub>2</sub> samples for FTIR in situ experiments were prepared as follows. The TiO<sub>2</sub> water suspension treated with ultrasound during 15 min time interval was uniformly deposited onto the CaF<sub>2</sub> glass (diameter 20 mm and thickness 1 mm) and dried at room temperature. The TiO<sub>2</sub> powder density in obtained samples was  $\approx 1 \text{ mg/cm}^2$ .

These samples were placed in the thermostatic reactor mounted in the cell compartment of FTIR spectrometer (Thermo, NICOLET 380) which was described previously [19]. The main feature of the reactor is the possibility of measuring either IR spectra of the gas phase or the TiO<sub>2</sub> catalyst surface with adsorbed species during the PCO process. All IR spectra were measured in the 900–4000 cm<sup>-1</sup> region with the 2 cm<sup>-1</sup> resolution and the accumulation of 16 scans. All experiments were carried out in atmosphere of air cleared from CO<sub>2</sub> and water. Therefore in all

experiments oxygen with a percentage of 23 mass% was contained. An airflow of 100 cm<sup>3</sup>/min of  $\approx 0\%$  relative humidity was passed through the reactor with the installed sample for 1 h. Then, 1 ml of gaseous NH<sub>3</sub> at 1 bar pressure was usually injected into the reactor before PCO. Relative humidity  $\approx 0\%$  was used for this purpose that all experiments passed in identical conditions.

The high pressure Hg lamp DRSH-1000 (Russia) was used as UV light source. Sample irradiation was conducted by condensed light passed through water filter (major line  $\lambda \sim 365 \text{ nm}$ ,  $W = 20.8 \text{ mW/cm}^2$ ). The measurement of light intensity was conducted by the microvolt meter F-136 (Russia) equipped with the semiconductor light intensity detector calibrated with the ferrioxalate actinometer [20].

### 2.4. Surface species analysis

The detection of final products and intermediates of the NH<sub>3</sub> PCO adsorbed on the photocatalyst surface was conducted by the analysis of water rinsed from the photocatalyst. The ion chromatography method with Metrohm 861 (Advanced Compact IC) instrument was used for rinsing water analysis and detecting inorganic ions. Eluent was 3.2 mM Na<sub>2</sub>CO<sub>3</sub>, 1.0 mM NaHCO<sub>3</sub>, volume of selected test 20 μL, flow rate 0.7 ml/min in column A supp 5 (250/4.0 mm).

The rinsing of surface species was done according to the following method. A 3 mg of deposited photocatalyst was gently transferred from the CaF<sub>2</sub> glass support into the 20 ml glass beaker and then the 10 ml of deionized water was added. Then the suspension was sonicated for the 5 min time interval and left for 1 h for surface species desorption. To be assured of full removal ions from the surface, the measurement of adsorption these ions on the catalyst surface in similar conditions has been made. The metering curve has been constructed using results of adsorption.

## 3. Results and discussion

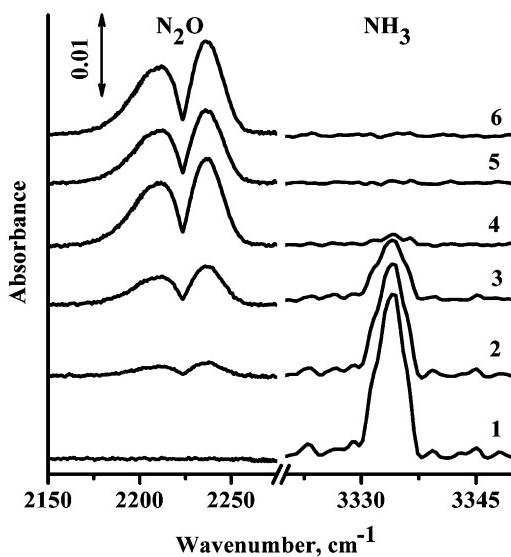
### 3.1. FTIR study of NH<sub>3</sub> PCO with the pure unmodified TiO<sub>2</sub>

After the injection of 1 ml gaseous NH<sub>3</sub> (pressure 1 bar) into the IR cell and subsequent setting of the adsorption equilibrium between gas phase and photocatalyst surface the sample irradiation was started and the IR spectra of gas phase and photocatalyst surface were registered periodically for PCO results monitoring. As measurement of concentration, we used "ppm" as one million part of atmospheric pressure.

Fig. 1 demonstrates the changes of gas phase IR spectra during NH<sub>3</sub> PCO on the pure unmodified TiO<sub>2</sub>. The 3336 cm<sup>-1</sup> absorption band corresponds to the valence symmetrical vibration  $\nu_s(\text{N-H})$  in the NH<sub>3</sub> molecule whereas 2224 cm<sup>-1</sup> absorption band corresponds to the valence symmetrical vibration ( $\nu_s$ ) in the N<sub>2</sub>O molecule [21]. The formation of water could be seen from the rotational component of the same gaseous IR spectra in the 3550–3900 cm<sup>-1</sup> range where the increase of  $\nu(\text{O-H})$  absorption bands intensities corresponds to the gaseous water formation. So the formation of gaseous N<sub>2</sub>O and H<sub>2</sub>O and ammonia disappearance during the NH<sub>3</sub> PCO with the pure unmodified TiO<sub>2</sub> was observed in the gas phase.

Using the integral form of Lambert's absorption law<sup>1</sup> it is possible to calculate the concentrations of gaseous NH<sub>3</sub> and N<sub>2</sub>O from the IR spectra (Fig. 1) [22].  $A_0$  values for ammonia and nitrous oxide were determined in separate experiment and turned out to be  $A_{0(3320-3341 \text{ cm}^{-1})} = 2.664 \times 10^{-6} \text{ ppm}^{-1} \text{ cm}^{-2}$  and  $A_{0(2150-2260 \text{ cm}^{-1})} = 4.722 \times 10^{-4} \text{ ppm}^{-1} \text{ cm}^{-2}$  for NH<sub>3</sub> and N<sub>2</sub>O, respectively. The obtained data from IR spectra gave us the

<sup>1</sup>  $A = A_0Cl$ , where  $A$ : the area of an absorption band (cm<sup>-1</sup>),  $l$ : optical pathlength (cm),  $C$ : gas concentration (ppm) and  $A_0$ : aspect ratio (ppm<sup>-1</sup> cm<sup>-2</sup>).

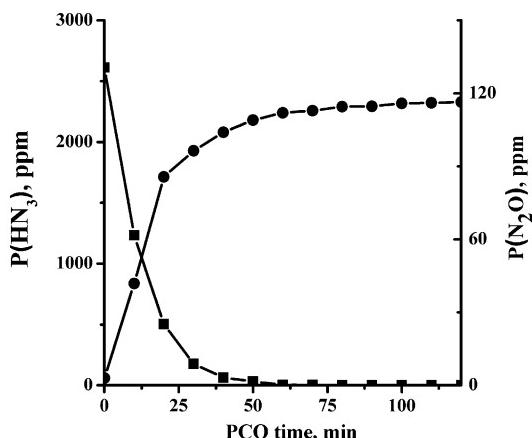


**Fig. 1.** FTIR spectra of the gas phase during the 1 ml NH<sub>3</sub> portion PCO in the IR cell ( $T = 293\text{ K}$ , relative humidity  $\approx 0\%$ , reactor volume 300 ml). Figures above spectra correspond to the following times of measurement: 1, before irradiation was started; 2, 15 min; 3, 30 min; 4, 60 min; 5, 90 min; 6, 120 min.

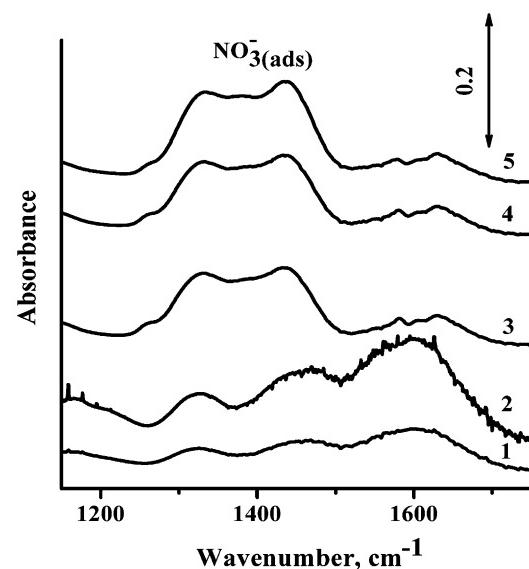
typical kinetic of N<sub>2</sub>O accumulation and NH<sub>3</sub> disappearance during the TiO<sub>2</sub> mediated ammonia PCO (Fig. 2). The initial NH<sub>3</sub> pressure is  $P_0 \approx 2600\text{ ppm}$  before irradiation was started whereas calculated initial pressure  $P_{\text{calc}}$  should be equal to 3330 ppm in the absence of adsorption. It means that about 730 ppm or 22% of injected ammonia was adsorbed on the TiO<sub>2</sub> surface in the beginning.

The complete removal of ammonia occurs for the first 60 min of PCO resulting in the formation of  $P_{\text{fin}} = 120\text{ ppm}$  of gaseous N<sub>2</sub>O. If one will calculate the conversion of ammonia into N<sub>2</sub>O one should take into account that each N<sub>2</sub>O molecule consists of two nitrogen atoms so the conversion ratio ( $\alpha$ ) will be in our case  $\alpha(\text{N}_2\text{O}) = (2P_{\text{fin}}(\text{N}_2\text{O})/P_{\text{calc}}(\text{NH}_3)) \times 100\% = (2 \times 120/3330) \times 100\% = 7.2\%$ .

The formation of adsorbed nitrates was also observed according to IR spectra of the TiO<sub>2</sub> surface during the NH<sub>3</sub> PCO (Fig. 3). It was demonstrated in the previous work [13] that the absorbance in TiO<sub>2</sub> surface IR spectra in the 1280–1500 cm<sup>-1</sup> range with the maximums at the 1350 cm<sup>-1</sup> (bidentate [23]) and 1440 cm<sup>-1</sup> (monodentate [24]) corresponds namely to HNO<sub>3</sub> adsorbed on the TiO<sub>2</sub>. It is only possible to obtain the qualitative information about



**Fig. 2.** Kinetic curves of NH<sub>3</sub> (■) vapor removal and N<sub>2</sub>O (●) accumulation during the 1 ml gaseous NH<sub>3</sub> PCO. Experimental conditions are the same as indicated in the caption for Fig. 1.



**Fig. 3.** FTIR spectra of the unmodified TiO<sub>2</sub> surface during the PCO of 1 ml gaseous NH<sub>3</sub> in the 300 ml static reactor.  $T = 293\text{ K}$ , relative humidity  $\sim 0\%$ . Figures above spectra correspond to the following times of measurement: 1, before irradiation was started; 2, 30 min; 3, 60 min; 4, 90 min; 5, 120 min.

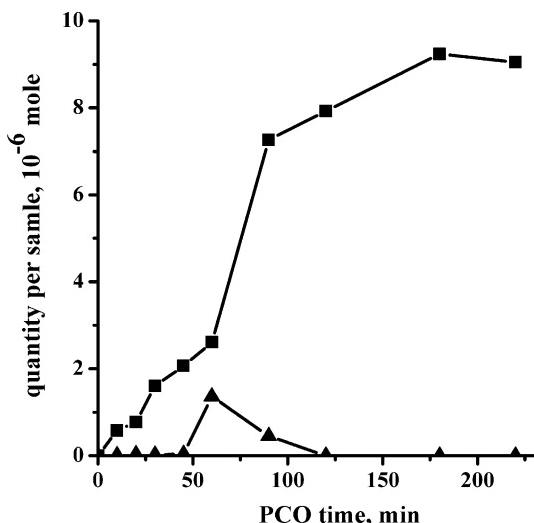
the HNO<sub>3</sub> quantity on the photocatalyst surface during NH<sub>3</sub> PCO and its dynamics. A new band at 1624 cm<sup>-1</sup> appeared under photoirradiation and grew with time of irradiation. It is well known that this band is assigned to the deformation vibration of H<sub>2</sub>O or OH groups interacting with monodentate or bidentate nitrate [25]. In spectra 1 and 2 (Fig. 3) corresponding to the beginning of PCO wide absorption bands near 1600 and 1460 cm<sup>-1</sup> are corresponding to the deformation vibrations in the NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> species. The last one forming on the TiO<sub>2</sub> surface as a result of NH<sub>3</sub> interactions with surface Bronsted acid sites.

A series of identical PCO experiments with equal NH<sub>3</sub> portions and photocatalyst samples was conducted to measure the quantitative kinetics of adsorbed species on the photocatalyst surface. Each PCO run was stopped at different times and the surface species analysis with liquid ion chromatograph was conducted. Only nitrates and nitrites were found and kinetics of their quantities change is shown in Fig. 4.

Surface nitrates (NO<sub>3</sub><sup>-</sup>) being an intermediate reached its maximum quantity 60 min after the beginning of PCO reaction and completely disappeared after 65 min. Surface nitrate is the product of complete NH<sub>3</sub> mineralization and its quantity constantly rises during PCO and reached its final value  $v_{\text{fin}}(\text{NO}_3^-) = 9.3 \times 10^{-6}\text{ mol}$  200 min after the beginning of PCO reaction (Fig. 4).

Equal volumes (1 ml at 20 °C) of gaseous NH<sub>3</sub> were used in all experiments; it means that initial NH<sub>3</sub> quantity was equal to  $v_0(\text{NH}_3) = ((10^{-3} \text{ l}) \times 1 \text{ (atm)})/(0.082 \text{ l atm/mol K}) \times 293 \text{ (K)} = 4.2 \times 10^{-5}\text{ mol}$  in all cases. In this way the ammonia conversion ratio into nitrates is equal to  $\alpha(\text{NO}_3^-) = (v_{\text{fin}}(\text{NO}_3^-)/v_0(\text{NH}_3)) \times 100\% = (9.3 \times 10^{-6}/4.2 \times 10^{-5}) \times 100\% = 22\%$ .

The combination of TiO<sub>2</sub> surface IR spectra with the results of surface species analysis by means of ion chromatography allows further to use only IR spectroscopy for the approximate determination of the adsorbed nitrate quantity as a less laborious technique. In fact the area of the NO<sub>3</sub><sup>-</sup>(ads) absorption band in the 1228–1520 cm<sup>-1</sup> range is equal to  $S_{1228-1520}(\text{NO}_3(\text{ads})^-) = 43.8\text{ cm}^{-1}$  (Fig. 3, spectrum 5) and corresponds to the complete ammonia mineralization with the formation of  $9.3 \times 10^{-6}\text{ mol}$  of adsorbed nitrates according to ion chromatographic analysis (Fig. 4). On the basis of Lambert's absorption law one can suppose that the quantity of formed adsorbed nitrates  $v(\text{NO}_3(\text{ads})^-)$  could be expressed through the intensity of the corresponding absorption



**Fig. 4.** Kinetic curves of adsorbed nitrates  $\text{NO}_3^-$  (■) and nitrites  $\text{NO}_2^-$  (▲) quantities change during the 1 ml gaseous  $\text{NH}_3$  PCO on the pure unmodified  $\text{TiO}_2$ . Experimental conditions are the same as indicated in the caption for Fig. 1.

band via formula:

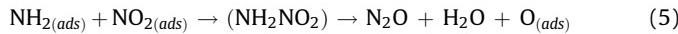
$$\begin{aligned} v(\text{NO}_{3\text{(ads)}}^-) \text{ (mol)} &= \frac{9.3 \times 10^{-6} \text{ mol}}{43.8 \text{ cm}^{-1}} \times S_{1228-1520}(\text{NO}_{3\text{(ads)}}^-) \\ &= 2.1 \times 10^{-7} \\ &\quad \times S_{1228-1520}(\text{NO}_{3\text{(ads)}}^-) \text{ (cm}^{-1}) \end{aligned} \quad (4)$$

Of course formula (4) could be applied only for photocatalyst based on the  $\text{TiO}_2$  with minor modifications (<1%) prepared by the same method described in the experimental part.

Since no other nitrogen containing species were detected in the gas phase and on the  $\text{TiO}_2$  surface then the last product of  $\text{NH}_3$  PCO should be dinitrogen ( $\text{N}_2$ ) and  $\text{NH}_3$  conversion ratio into  $\text{N}_2$  is equal to  $\alpha(\text{N}_2) = 100\% - \alpha(\text{N}_2\text{O}) - \alpha(\text{NO}_3^-) = 70.8\%$ . Lee et al. [26] managed to achieve 80% conversion ratio of  $\text{NH}_3$  into  $\text{N}_2$  but in water phase PCO using Pt modified  $\text{TiO}_2$ .

Let us compare kinetics of gaseous and surface species (Figs. 2 and 4). On the one hand the ammonia was completely removed from the gas phase after 60 min of PCO reaction and  $\text{N}_2\text{O}$  pressure reached almost stable level. On the other hand the quantity of the surface  $\text{NO}_3^-$  species reached only about 40% of its maximum and still was increasing. It means that there was still source of nitrogen somewhere in the reaction system which was transformed into adsorbed nitrates and probably into dinitrogen ( $\text{N}_2$ ) because the last product was not controlled during the PCO reaction.

It is known that particle  $\text{NH}_2$  reacts with  $\text{NO}_2^-$  (nitrites) on the surfaces of the catalyst with the formation of particle  $\text{NH}_2\text{NO}_2$  that is oxidized to  $\text{N}_2\text{O}$  [27]:

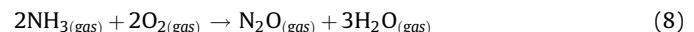
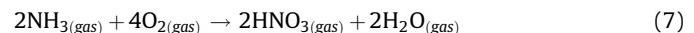
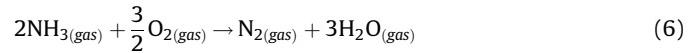


According to the Ramis et al. [28] the adsorption band wave number which could be assigned to the NO-stretching vibration in  $\text{NH}_2\text{NO}$  surface species is equal to  $1468 \text{ cm}^{-1}$  but in our case (Fig. 3) there is a wide adsorption band corresponding to the adsorbed nitrous acid. This wide band could mask the  $1468 \text{ cm}^{-1}$  adsorption band.

Therefore, after the removal of ammonia from the gas phase the increase in  $\text{N}_2\text{O}$  stops. At the same time the oxidation of intermediate products to nitrites and finally to nitrates occurs. Therefore, while studying washouts from the surface of the catalyst, we did not observe any nitrites during the initial moment but when the ammonia completely disappears from a gas phase

the formation of surface nitrates begin. Finally the nitrates are oxidized to nitrates which are the only surface products of complete  $\text{NH}_3$  PCO.

Based upon the above discussion it could be concluded that ammonia PCO reaction can proceed in three parallel routes giving  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{HNO}_3$  as major nitrogen containing products:



Gibbs free energy for these three reactions  $\Delta_r G_{298}^0$  was calculated on the basis of data presented in Ref. [30] and turned out to be  $-652.41$ ,  $-585.4$  and  $-548.31 \text{ kJ/mol}$  for reactions (6), (7) and (8) correspondingly. The real  $\Delta_r G_{298}^0$  value for reactions (6)–(8) should be somewhat lower because some components of reactions and especially nitric acid could adsorb on the catalyst surface but nevertheless as one can see all three products could be formed since there is no thermodynamic prohibition. Moreover, the more profitable reaction is from the thermodynamic point of view the higher is the conversion ratio of ammonia into the corresponding product. Indeed the  $\text{N}_2$  is the major product ( $\alpha(\text{N}_2) = 70.8\%$ ) and  $\Delta_r G_{298}^0$  for it is equal to  $-652.41 \text{ kJ/mol}$  and vice versa  $\text{N}_2\text{O}$  is the minor product and  $\Delta_r G_{298}^0$  for it is equal to  $-548.31 \text{ kJ/mol}$  is the lowest one.

### 3.2. Ammonia PCO with $\text{TiO}_2$ modified by noble metals and transition metal oxides

Studies of gaseous ammonia PCO using several modified  $\text{TiO}_2$  photocatalysts were done analogously with the investigation of ammonia PCO on the unmodified  $\text{TiO}_2$  reported in the previous section.

Generally two types of  $\text{TiO}_2$  based photocatalysts were studied namely (1)  $\text{TiO}_2$  modified with noble metals (Ag, Au, Pd, and Pt) deposited by chemical or photochemical reduction method; and (2)  $\text{TiO}_2$  modified with transition metal oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{NiO}$ ,  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$ ). The purpose of both types of  $\text{TiO}_2$  modifications was to improve the  $\text{TiO}_2$  adsorption properties against gaseous  $\text{NH}_3$  and therefore to raise the rate of ammonia PCO. Modification of  $\text{TiO}_2$  with sulfuric acid purposed the same object. Another aim was to reduce the nitrous oxide output.

Sano et al. [31] used Ag/ $\text{TiO}_2$  photocatalyst for the  $\text{N}_2\text{O}$  photocatalytic decomposition but in the presence of methanol vapor. Some other researchers like Satsuma et al. [32] and Henderson et al. [33] investigated the catalytic activity of some transition metal oxides in the nitrous oxide decomposition reaction. As in work [32] they also used reducing agent but methane instead of methanol. Oxygen turned out to inhibit  $\text{N}_2\text{O}$  decomposition reaction due to the lack of oxygen vacancies in metal oxide phase which is necessary for the removal of oxygen from  $\text{N}_2\text{O}$  molecule and the formation of molecular nitrogen. Such oxygen vacancies were found to influence the  $\text{N}_2\text{O}$  decomposition in high vacuum and cannot be formed in ambient conditions because air always contains up to 20% of  $\text{O}_2$ . Also the several hundred degree temperatures were needed to achieve the acceptable decomposition rate.

Nevertheless we tried to use  $\text{TiO}_2$  based photocatalysts in ambient conditions without the addition of reducing agent to understand the possibility of minimizing the  $\text{N}_2\text{O}$  output during the  $\text{NH}_3$  PCO. All results are summarized in Table 1.

The highest activity and ammonia conversion into  $\text{N}_2$  and the lowest nitrous oxide output were demonstrated by unmodified high surface area  $\text{TiO}_2$  (anatase). Therefore it is the best

**Table 1**

Catalytic activity of different  $\text{TiO}_2$  samples during the 1 ml gaseous ammonia (calculated initial  $\text{NH}_3$  pressure  $P_{\text{calc}} = 3330 \text{ ppm}$ ) PCO in 300 ml static reactor (relative humidity  $\approx 0\%$ ,  $T = 293 \text{ K}$ ,  $W_{\lambda \approx 356 \text{ nm}} = 20.8 \text{ mW/cm}^2$ ).

Catalyst	Preparation method	Initial $\text{NH}_3$ pressure, $P_0$ (ppm)	NH <sub>3</sub> PCO rate for 30 min starting time interval (ppm(NH <sub>3</sub> )/min)	Part of oxidized NH <sub>3</sub> for 240 min time interval (%)	Ammonia conversion ratio ( $\alpha$ ) for 240 min time interval (%) into:		
					$\text{N}_2\text{O}$	$\text{NO}_3^{-\text{(ads)}}$ based on the surface IR spectra	$\text{N}_2$
$\text{TiO}_2$	Unmodified	2610	80.4	100	7	22	71
1% Ag( $h\nu$ )/ $\text{TiO}_2$	Photoreduction	2510	27.6	100	14	11	75
1% Ag( $\text{NaBH}_4$ )/ $\text{TiO}_2$	Chemical reduction with $\text{NaBH}_4$	2630	23.3	100	16	11	73
1% Au( $h\nu$ )/ $\text{TiO}_2$	Photoreduction	3030	26.8	100	27	11	62
1% Au( $\text{NaBH}_4$ )/ $\text{TiO}_2$	Chemical reduction with $\text{NaBH}_4$	2610	31.8	100	28	24	48
1% Pd/ $\text{TiO}_2$		2360	49.8	100	11	33	56
0.2% Pt/ $\text{TiO}_2$		2800	35.9	100	10	31	58
4M $\text{H}_2\text{SO}_4$ / $\text{TiO}_2$	Pretreated with 4M $\text{H}_2\text{SO}_4$ water solution	2840	68.5	100	8	27	65
1% NiO/ $\text{TiO}_2$	Impregnation with water solution of the corresponding metal salt with following calcinations	3040	2.9	35.55	2	1	97
0.1% $\text{Fe}_2\text{O}_3$ / $\text{TiO}_2$		3290	31.8	100	10	86	4
0.5% CoO/ $\text{TiO}_2$		3150	4.8	37.01	2	24	74
0.01% $\text{Fe}_2\text{O}_3$ / $\text{TiO}_2$		3280	39.8	100	10	20	70
0.01% $\text{MoO}_3$ / $\text{TiO}_2$		3200	20.8	100	9	53	38
0.01% $\text{V}_2\text{O}_5$ / $\text{TiO}_2$		3120	18.9	100	9	36	55

photocatalyst for being used in commercial air purifiers for ammonia decomposition.

Photocatalysts modified with noble metals with the following chemical or photochemical reduction demonstrated average activity, i.e. the ammonia could be mineralized completely for 4 h time period but the rate of mineralization is lower than for pure  $\text{TiO}_2$  and the  $\text{N}_2\text{O}$  production is also higher. The third column in Table 1 shows initial ammonia pressures after the adsorption equilibrium was established in the system. We anticipated the increase of photocatalyst adsorption properties against  $\text{NH}_3$  after the metal deposition but it was not observed because the quantity of adsorbed  $\text{NH}_3$  ( $P_{\text{calc}} - P_0$ ) was approximately the same as in the pure  $\text{TiO}_2$  case. Possible explanation of this fact is that the stability constants of noble metals complexes with ammonia are not high unlike the case with cyanide anions as ligand. That is why in our previous work we successfully used Au and Ag for  $\text{TiO}_2$  modification and obtained new very active photocatalysts for HCN PCO [18] but in this work the same approach failed.

All the photocatalysts which contained a lot of additional metal oxide phase (1% NiO/ $\text{TiO}_2$ , 0.1%  $\text{Fe}_2\text{O}_3$ / $\text{TiO}_2$  and 0.5% CoO/ $\text{TiO}_2$ ) demonstrated very low photocatalytic activity and initial  $\text{NH}_3$  PCO rate ( $<5 \text{ ppm/min}$ ). At the same time the ammonia adsorption on these samples is also very low because the initial pressure is close to theoretically calculated; it means that the metal oxide phases (NiO,  $\text{Fe}_2\text{O}_3$  or CoO) block the surface and prevent the ammonia interaction with the photocatalyst active sites.

Photocatalytic activity of photocatalysts containing 0.01% of additional metal phase ( $\text{Fe}_2\text{O}_3$ / $\text{TiO}_2$ ,  $\text{MoO}_3$ / $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$ / $\text{TiO}_2$ ) becomes higher but still about 2–3 times lower than for pure unmodified  $\text{TiO}_2$ . Probably the same blocking of the  $\text{TiO}_2$  surface occurs like in the previous case but to a lesser degree.

Practically for all active photocatalysts about 20–30% of initial ammonia is converted into nitrates and 10–30% into nitrous oxide. Overall conclusion could be made that the closer photocatalyst formula is to the pure high surface area anatase form  $\text{TiO}_2$  the more active it would be in the PCO reaction of ammonia.

### 3.3. Study of $\text{TiO}_2$ stability

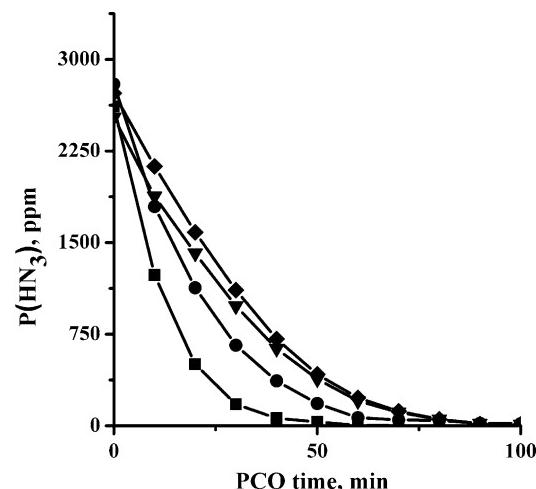
Finally we tested the stability of the best revealed photocatalyst which turned out to be purely unmodified  $\text{TiO}_2$  in multiple long

time ammonia PCO experiments. It was demonstrated that a photocatalyst deactivation occurs during several PCO runs (Fig. 5).

The deactivation of photocatalyst may develop due to the decrease of the number of active surface sites available for the reaction in several consecutive batch runs over the photocatalyst.

One can see that the  $\text{NH}_3$  conversion level remained unchanged and is equal to 100%, although the conversion time necessary to reach this level increased from 50 to 100 min for five PCO runs. The surface nitric acid accumulating during PCO that could be easily detected by the rising of absorption bands in the surface FTIR spectra at 1350 and  $1440 \text{ cm}^{-1}$  positions is responsible for such deactivation.

In this way 5 ml or  $2.1 \times 10^{-4} \text{ mol}$  of  $\text{NH}_3$  was photocatalytically oxidized by 3 mg or  $3.75 \times 10^{-5} \text{ mol}$  of  $\text{TiO}_2$ . It means that each Ti atom worked at least 5.6 times and could work some more. We suppose that the washing of photocatalyst could restore its photoactivity because adsorbed nitric acid was completely removed from the  $\text{TiO}_2$  surface during our nitrates measurements in water washed from used  $\text{TiO}_2$ .



**Fig. 5.** Kinetic curves of gaseous  $\text{NH}_3$  removal during several consecutive PCO runs of equal 1 ml  $\text{NH}_3$  portions in the 300 ml static reactor using pure unmodified  $\text{TiO}_2$ . Symbols ■, ●, ▼, ◆ are corresponding to the first, second, fourth and fifth oxidation runs.

#### 4. Conclusions

The ammonia PCO was investigated for a set of photocatalysts modified with noble metals and transition metal oxides.

Nitrous oxide N<sub>2</sub>O was registered as the gaseous PCO product. The formation of dinitrogen N<sub>2</sub> another gaseous PCO product was estimated from the mass balance. Adsorbed nitrites NO<sub>2</sub><sup>-</sup> and nitrates NO<sub>3</sub><sup>-</sup> were registered as surface intermediates and final products of NH<sub>3</sub> PCO.

The best activity was demonstrated by unmodified high surface area anatase from TiO<sub>2</sub>. This photocatalyst also demonstrated the lowest N<sub>2</sub>O production during PCO which is also very important positive feature from the practical point of view. Ammonia was converted into N<sub>2</sub>O (7%), N<sub>2</sub> (71%) and adsorbed HNO<sub>3</sub> (22%) by this photocatalyst.

The accumulation of surface nitrates is the possible reason of TiO<sub>2</sub> deactivation during the several consecutive runs of NH<sub>3</sub> PCO. Nevertheless every Ti atom worked at least 5.6 times till the PCO rate decreased in two times.

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